

Engineering Performance and Material Viscoelastic Analyses Along a Compounding Line for Silica-Based Compounds. I. Mixing Line Performance Analysis

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ABSTRACT: In the tire industry, the preparation of silica-filled compounds requires relatively complicated compounding operations, which involve several dumping, cooling, and remixing steps, to eventually obtain quality final batches. The various and complex sets of events that take place along the mixing line remain, however, poorly understood. The objectives of this study, reported in two companion articles, were to deepen the understanding of silica–silane compounding operations. Two approaches were used in parallel: first, we performed a deep analysis of the engineering performance of an existing—and successful—mixing line by paying attention to the various curves that are nowadays recorded during internal mixing, and second, we studied the variations of the nonlinear viscoelastic properties along the mixing line using so-called Fourier transform rheometry, implemented on a commercial torsional dynamic rheometer. The first article of the se-

ries is devoted to the performance analysis of the mixing line through mixing trials along an industrial line. Silica dispersion and the treatment with silane were initiated during a master-batching process; then, two remixing steps were performed to achieve the right silanization degree. Curatives were added during a final mixing step. Mixing signatures, containing information such as mixing power, ram position, compound temperature, and rotor speed, gave some insight to the dispersion–silanization processes and, among other results, showed that the dumping, cooling, and remixing of the compound comprised a more efficient process than the maintenance of a very high batch temperature for an extended time, essentially because one could make use of stress-induced dispersing effects. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 942–952, 2009

Key words: compounding; mixing; rubber; silicas

INTRODUCTION

With respect to the advantages offered in terms of lower viscous dissipation and, hence, fuel savings, high-structure silica is increasingly used instead of carbon black in the compounding of certain tire components. However, silica and carbon black reinforcements are totally different, and the former requires a chemical modification of the particle surface, essentially to tamper its hydrophilic character and, hence, favor dispersion in hydrophobic elastomers and to achieve the development of appropriate interactions with the rubber matrix. Such a modification is achieved by the treatment of silica particles with special chemicals, for instance, difunctional silanes. Although silanated silica is commercially available, *in situ* silanization (i.e., during mixing) has become the standard practice in the tire industry over recent decades.

The preparation of silica-filled compounds is by far the most complex mixing operation in tire technology, essentially because the silanization process is carried out in internal mixer, concomitantly with the dispersion of filler particles and other compounding ingredients. In other words, a chemical reaction must be activated and completed in a highly viscous medium. The order of addition of the formulation ingredients and the control of the mix temperature variation through shear warm-up are important aspects of the process, likely typical of the mixing line considered and essential know how, about which tire manufacturers remain quite discreet. Little is really known about the complex physical events (i.e., filler particle dispersion and distribution) and chemical events (i.e., silane–silica reactions) that take place in the earlier steps of such compounding operations, essentially because direct observations are really challenging, if not impossible.¹ In quite a practical manner, rubber engineers have set up relatively complicated compounding operations for silica–silane-filled formulations, which involve several dumping, cooling, and remixing steps, to eventually obtain quality final batches. The

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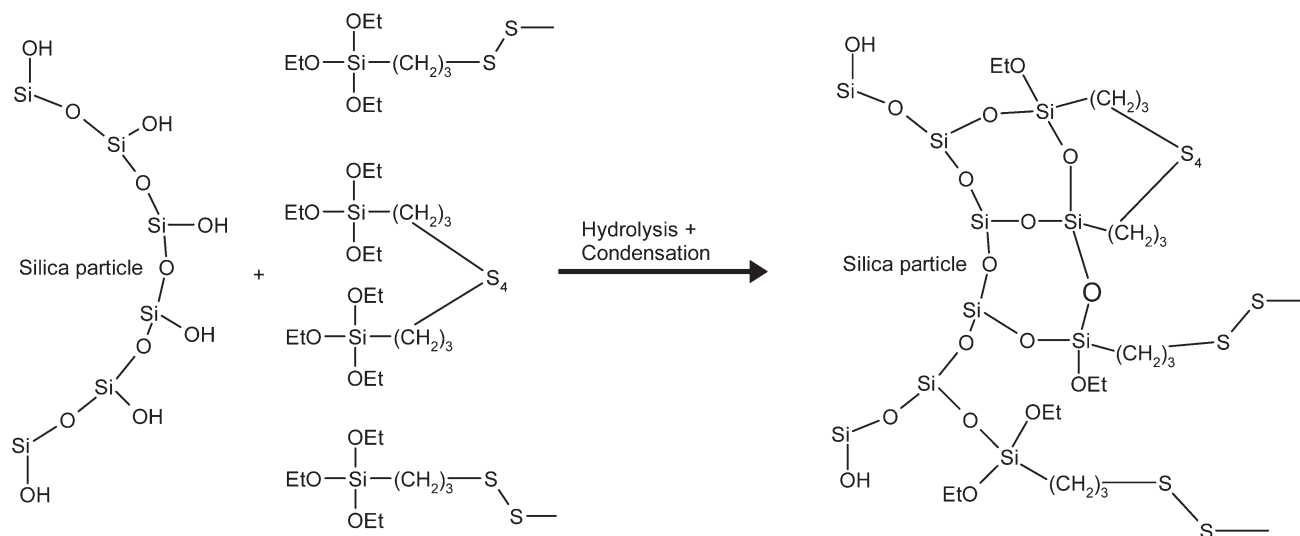


Figure 1 Chemical reaction equation of the silanization process.

objectives of this study were to deepen the understanding of the various and complex set of events that take place along an industrial mixing line for silica-based compounds.

Two approaches were used in parallel: first, we performed a deep analysis of the engineering performance of an existing—and successful—mixing line by paying attention to the various curves that are nowadays recorded during internal mixing, and second, we studied the variations of the nonlinear viscoelastic properties along the mixing line using so-called Fourier Transform rheometry, implemented on a commercial torsional dynamic rheometer. By comparing results and conclusions from both approaches, we expected, and have indeed obtained, a better understanding of the complexity of the process. The first article of the series is devoted to the performance analysis of the mixing line.

Requirements for a well-mixed silica-based compound

Today, modern tires have to meet very demanding handling requirements with respect to grip and skid under wet, snowy, or icy conditions. Rolling resistance must be as low as possible, and a high mileage becomes more important because of environmental reasons. It is, therefore, necessary to use silica-filled tread compounds based on solution styrene-butadiene rubber (SSBR) and high-cis polybutadiene (BR) polymers in high-performance tires.² The compound is reinforced by means of a silica-silane system. The silica replaces the traditionally used carbon black, and the (organo)silane [e.g., TESPT or bis(triethoxysilylpropyl)tetrasulfane] acts as a coupling agent between silica and the polymers after vulcanization. The chemical bonding between silica and the poly-

mers is complicated, and at least two chemical reactions are needed to achieve full filler-rubber interactions. One of them is an *in situ* reaction between the silane and the silica, which takes place during the mixing process.¹ The corresponding reaction scheme is given in Figure 1.

A typical formulation of a tread compound was given by Rauline.³ The compound was based on a blend of SSBR and BR, highly dispersible silica as a filler, silane (TESPT), and process oil. In the tire industry, several modifications have been brought to this basic formulation. For instance, natural rubber might be added to improve the tire performance and/or the processability of the compound, and new generations of silane, such as VP Si363 from Evonik⁴ or the NXT silane family of GE Silicones OSI Specialties,⁵ have also been introduced on the market.

During the mixing process of these compounds, all ingredients should be well distributed and dispersed to obtain a good quality compound, even on a microscopic level. Contrary to the mixing process of carbon black compounds, not much is known about how the required degree of silica dispersion should be achieved, which, of course, leaves room for pragmatic engineering. Because silica is highly hydrophilic, it is difficult to wet the silica surface with gum rubbers for tire application because most of them have a hydrophobic nature. Reuvekamp⁶ investigated the dispersion mechanism of silica through a series of well-designed experiments with different silanes to get a maximum microdispersion. It is well known that the lower the dynamic stress softening (i.e., the so-called Payne effect) is, as measured on an (uncured) compound at 100°C, the better the microdispersion (10 nm–1 μm) of the filler will be. This property is usually measured by means of a closed-chamber dynamic rheometer, such as the

RPA 2000 rubber process analyzer (Alpha Technologies, Ltd., now a division of Dynisco LLC, Franklin, MA) The elastic modulus (G') of the sample, as measured at 100°C at a frequency of 0.5 Hz and increasing amplitude, is considered representative for the compound's Payne effect. From Reuvekamp's experiments, the following dispersion mechanism can be inferred:

- High shear forces in the mixing chamber break down the large silica granules or pearls into smaller agglomerates.
- Silane is moved to the surfaces of the silica, which consist of silanol groups.
- At sufficiently high temperatures (>120°C), one of the alkoxy-silyl moieties of silane reacts with a silanol group on the silica surface, which causes a hydrophobing effect.
- With proceeding hydrophobation (also called *silanization* of the silica surface), the dispersability of the filler in the rubber matrix increases, which enables the silica to be wetted with gum molecules.
- As side products of this chemical reaction, water and ethanol are formed.
- As soon as physical bonding between silica and the polymers exists, it enables a better or more efficient dispersion effect.
- Newly created hydrophilic surfaces are silanized consequently to reduce silica-silica interactions and to create the possibility of the formation of chemical bonds with polymer chains during vulcanization.

In addition, Dierkes¹ found that the degree of silanization, which can be obtained in a certain mixing process, is higher when the evaporation of the ethanol from the mixing chamber is forced. At temperatures higher than 160°C, a second, unwanted reaction may be observed that causes a scorch or prevulcanization effect in the compound. This is especially true for compounds containing TESPT.⁷

Consequently, a well-mixed silica compound should meet the following requirements:

- Lowest dynamic stress softening effect for best microdispersion.
- No (visible) undispersed silica in a light microscope sample of the compound.
- As homogeneous as possible, which shows that there are neither a major gradient in the degree of silanization nor scorched lumps.
- No porosity visible in the final compound (which shows that most of the ethanol and water has been evaporated).
- Highest batch to batch uniformity (necessary because rubber mixing is a batch process).

This article deals with a description of how the mixing process is designed in such a way that these requirements are fulfilled. In a second article, the development of the viscoelastic properties of a silica compound along the mixing process are investigated and discussed.

Mixing of silica compounds

The mixing of silica compounds is complicated because the silica has to be hydrophobated by means of silane, as stated before. This chemical reaction, also called the *silanization* reaction, lasts long with respect to standard mixing times, and moreover, the temperature cannot rise too high (it is said that the reaction temperature may not exceed 160°C to prevent secondary reaction effects.) It, therefore, requires one or two remilling phases to complete the silanization process. Temperature control in the mixing process is very important but difficult to realize; indeed, rubber polymers combine a very high viscosity and a low thermal conductivity. This means that the power, supplied to the mixer, is partly transformed in enthalpy through viscous dissipation under shearing conditions, and therefore, an increase in the compound temperature is observed during mixing. Small variations in batch weight and additive concentration in the compound result in variations in the mixing process between batches, and hence, the temperature increase. Silica compounds are mixed preferably in intermeshing mixers with variable and adjustable rotor speeds. Intermeshing mixers show a more preferred (cooling) surface-to-volume ratio.⁸ By lowering the rotor speed during mixing, one can somewhat reduce the temperature increase. Because the hydrophobation reaction is influenced by the content of ethanol (a splitoff product from this reaction) and the moisture content, one must lift the ram several times during one mixing cycle. A typical master-batch mixing cycle for SBR silica-silane compounds on a 320E internal mixer is shown later in Figure 5, in which one can clearly see that the temperature increase is limited by the lowering of the rotor speed.

The use of two subsequent roll mills in the downstream of such mixing lines is the preferred approach, especially when the roll mills are equipped with stock blenders (Fig. 2). After discharging, the rubber batch is sheeted on the two roll mills. By putting the sheet through the stock blender, the free surface from which the ethanol and moisture can be evaporated is rather large, which allows the chemical reaction to proceed even at somewhat lower temperatures. A study by Zuuring⁹ showed that a smaller mill clearance setting and a longer milling time resulted in better silanization conditions. This study also showed that by prompting two-roll milling after mixing in an intermeshing mixer, one can eliminate one remilling step, as illustrated in Figure 3.

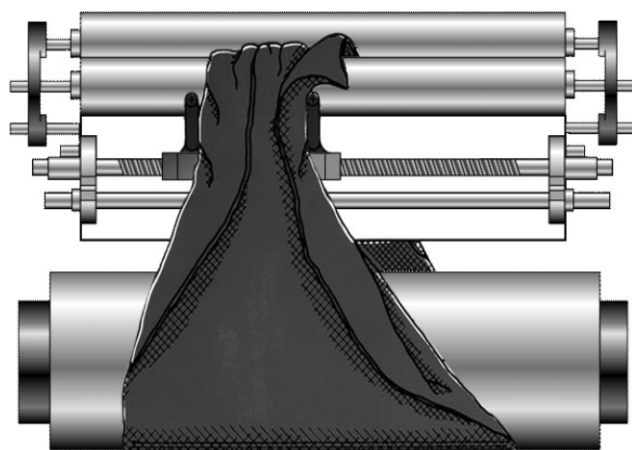


Figure 2 Two-roll mill with a stock blender.

Because of poor cooling conditions in the internal mixer, the silanization process cannot be completed within one mixing cycle. Often, one or more so-called remixing processes have to be performed before the curative addition during a final batch-mixing step. As soon as the compound contains curatives, the batch temperature should not exceed 115°C to prevent pre-vulcanization. At this temperature, however, no more efficient silanization processes can take place.

EXPERIMENTAL

Mixing trials were performed with a silica compound whose master-batch and final-batch formulations are given in Table I.

The first master-batch mixing step was done in a 320-L intermeshing mixer GK320E equipped with PES5 rotors, as manufactured by Harburg Freudenberger, Freudenberg, Germany (formerly W&P). The feeding of the materials was done automatically in the following way:

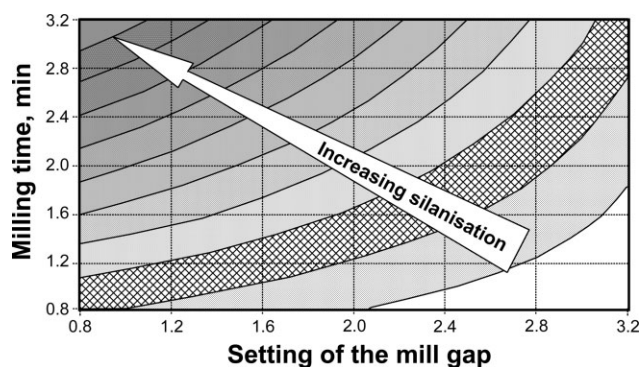


Figure 3 Influence of the open mill mixing process on the degree of silanization in an SSBR/silica/TESPT compound as shown in a contour plot of the Payne effect $[C'(0,56)]$ according to Zuuring.⁹ With the proceeding silanization, the Payne effect drops tremendously.

TABLE I
Formulation of the Silica Compound

Ingredient	Content (phr)
Master batch	230.3
Natural rubber (TSR20)	20
High-cis BR	20
SSBR (oil extended)	69.8
Highly dispersible silica	83.5
N375 carbon black	6.6
Silane TESPT	6.6
Processing oil	8.8
Processing promoter	4
Zinc oxide	3
Stearic acid	2
6PPD	2
TMQ	2
Protector wax	2
Final batch	
DPG	2
Accelerator	1.3
Sulfur	1.3
PVI	0.2

6PPD = N-1,3 (dimethylbutyl) N'-phenyl-p-phenylene diamine; TMQ = 2,2,4 trimethyl-1,2 dihydroquinoline, polymerized; PVI = *PreVulcanization Inhibitor*, common name standing for N-(cyclohexylthio) phtalimide.

- Polymers via a conveying belt.
- Carbon black and silica by means of an automated silo weighing system.
- Small chemicals by an automated silo weighing system with a small weighing range.
- Process oil, liquefied chemicals, and silane by means of two injection nozzles in the mixing chamber.

The temperatures of the mixer body and the rotors were set at 50°C. The rotor speed was varied continuously between 10 and 50 rpm. A fill factor of 0.571 was used.

The mixing process was controlled automatically, and the following signals were recorded and treated by means of an Oracle database (Oracle Corp., Redwood Shores, CA):

- Power supply.
- Ram position.
- Compound temperature (by means of a thermocouple on a side plate of the mixing chamber).
- Rotor speed.

A milling process in three pairs of two-roll mills, downstream of the internal mixer, followed the master-batch mixing process. The purpose of the first mill (2000 × 600 mm²) was to sheet out the content of the mixing chamber into a sheet roughly 20 mm thick, which was guided to the second mill (2000 × 600 mm²), which was equipped with a stock blender. The operator guided the lead end of the slab into the

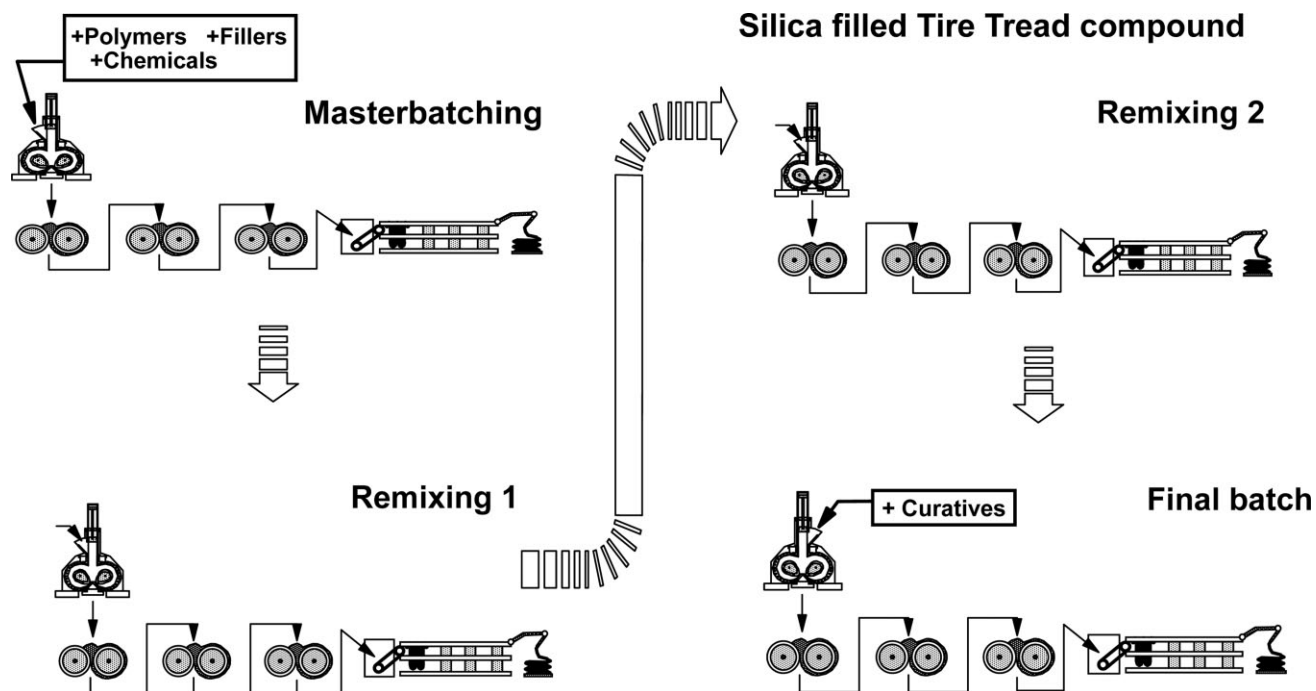


Figure 4 Schematic diagram of the mixing lines and processes.

stock blender, and during the cycle time of the next batch, the compound was mixed on the second mill. By means of a strip of approximately 400 mm wide, the stock was guided to the last mill ($1500 \times 450 \text{ mm}^2$). The last mill sheeted the compound into a well-defined thickness and width ($900 \times 10 \text{ mm}^2$), and the sheet was put into a batch-off machine to be dipped in an antitack soap and to cool to room temperature. Finally, the sheet was put wig wagged on a pallet for transport to the next mixer. All mills were set at a temperature of 60°C . The second two-roll mill was equipped with peripherally drilled cooling channels and operated with variable friction.

The master batch was remixed twice to obtain the right silanization degree. Such operations were done on a tangential mixer type GK 160 UK equipped with old standard rotors (supplied by Harburg Freudenberger, Germany). Mixing was conducted at a fixed rotor speed with friction (28/33 rpm), and the machine was run in automatic mode. Underneath the mixer, three pairs of two-roll mills were arranged as in the previous step (master-batch mixer); however, the first mill was a mixing one with a stock blending device. A fill factor of 0.651 was used for the internal mixer, whose body and rotors were kept at a temperature of 30°C .

The final-batch mixing was done on a similar mixing line. Master batches and small ethylene vinyl acetate bags containing weighed curatives were added to the mixer at the same time. Except the rotor speed, the same signals as in the master-batch mixing process were recorded continuously.

The mixing lines and procedures are schematically depicted in Figure 4.

The detailed mixing procedures are given in Tables II–IV.

RESULTS

Mixing fingerprints: Interest and uses

The general meaning of fingerprints to design a mixing cycle and to control the mixing process was presented in our earlier articles.^{10–13}

The fingerprint of the master-batch mixing cycle is given in Figure 5. The mixing process, given in

TABLE II
Procedure for Master-Batch Mixing

Step	Floating weight	Rotor speed	Action
1	Up	30	Feeding of polymers
2	Down	40	Mixing for 80 s
3	Up	30	Feeding fillers and small chemicals
4	Down	40	Mixing for 50 s
5	Down	25	Injection of fluid components
6	Up/down	20	Ram sweep
7	Down	20	Mixing for 40 s
8	Up/down	20	Ram sweep
9	Down	20	Mixing until 135°C
10	Up/down	20	Ram sweep
11	Down	20	Mixing until 150°C
12	Down	30	Discharge
13	Up	35	Waiting for next batch

TABLE III
Procedure for Remill Mixing

Step	Floating weight	Action
1	Up	Master-batch feeding
2	Down/up	Inverse ram sweep
3	Up	Mixing for 20 s
4	Down	Mixing until 140°C
5	Up/down	Discharge with ram sweep
6	Up	Waiting for next batch

Table II, was clearly recognized as a standard procedure. The mixing process started by the addition of the polymers into the mixing chamber, followed by movement down the ram. Almost immediately, the ram set on its lowest position because the mixing chamber was underfilled with only the gum polymers. The power input was rather low and decreased during the polymer-blending phase. After the ram was lifted, the filler (silica) was added. It then took around 30 s before the ram reached its lowest position. The total volume of the fillers exceeded the maximum remaining mixing chamber volume because the bulk density of silica was much lower than its material density. The power input was the highest during the total cycle, which pointed to high dispersion effects and probably strong particle–particle interactions. At about 220 s after the mixing process was started, the process oil was injected, together with the silane. The power input decreased almost immediately because, at the beginning, the process oil acted as a lubricant between the compound and the mixing chamber wall before it was incorporated. This obviously also meant an immediately lower efficiency of the filler

TABLE IV
Procedure for Final-Batch Mixing

Step	Floating weight	Action
1	Up	Master-batch and curative feeding
2	Down/up	Inverse ram sweep
3	Up	Mixing for 5 s
4	Down	Mixing for 20 s
5	Up/down	Ram sweep
6	Down	Mixing for 20 s
7	Up/down	Ram sweep
8	Down	Mixing until 105°C
9	Up/down	Discharge with ram sweep
10	Up	Waiting for next batch

dispersion process, followed by an increase in the power input as the oil and the silane were absorbed by the compound undergoing mixing.

The power input steadily increased until a maximum was reached then during the remaining mixing process; combined with the temperature increase, this pointed out a viscosity decrease of the compound because the power input decreased toward a plateau value. Either some silica remaining on top of the ram might have fallen into the compound or the dispersion process was still dominant and hiding the silanization effect. From around 340 s after the start of the mixing process, the silanization reaction was really observable because the compound temperature exceeded 120°C and enough activation energy was available to initiate silanization. The signal of the power input exhibited some fluctuations, which might have been caused by minor compound inhomogeneities.

Figure 6 shows three fingerprints for different batches out of the same run when the same

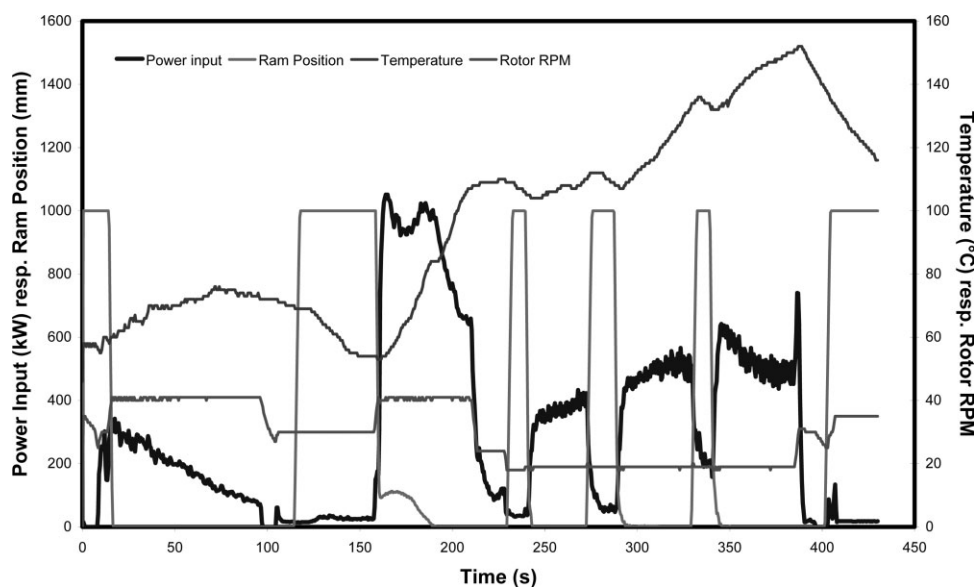


Figure 5 Fingerprint of the master-batch mixing cycle on a GK320E with PES5 rotors.

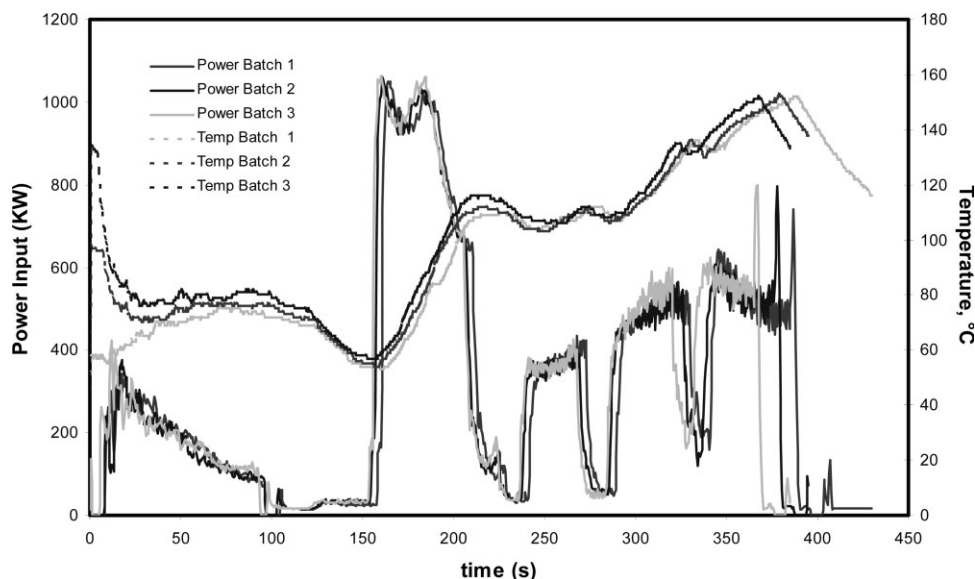


Figure 6 Fingerprints of three subsequent batches of the master-batch mixing process.

compound formulation was prepared. Only power input and temperature are shown. The power input of all three batches was similar, but some nonsteady conditions of the mixing process were clearly recognized in the temperature signals. The first batch was produced after a longer waiting time. Generally, the temperature signal of batch 2 was higher than of batch 1, and the temperature signal of batch 3 was higher than the signal of batch 2. The criterion to proceed to mixing step 10 (at approximately 330 s after the start of the mixing process) and to discharge was based on the compound temperature (refer to Table II), and its influence on the duration of the corresponding mixing time was clear. The total mixing time of batch 3 was about 20 s shorter than the total mixing time of batch 1. We expected that the degree of silanization of batch 1 would be somewhat higher than the corresponding degree of batch 3. We also expected that these differences would level off after the milling process, downstream of the internal mixer.

The fingerprints of the first remilling process are given in Figure 7. The mixing procedure, given in Table III, was easily recognized. After mixer feeding, the ram was moved downward and upward to push the rubber slab into the mixing chamber and to allow all the master batch to be fed in the mixer. The power supply was, therefore, rather high at the beginning of this mixing step but decreased with elapsed time. The effect of the ram position was almost undetectable in batch 1 and 2. The power input and the temperature were hardly influenced as soon as the ram reached its lowest position. This means that the rubber stock was well kept in the mixing chamber during the operation.

In sharp contrast, a huge effect on the power input was seen in batch 3 as soon as the ram was lifted (between 60 and 80 s after the start of the

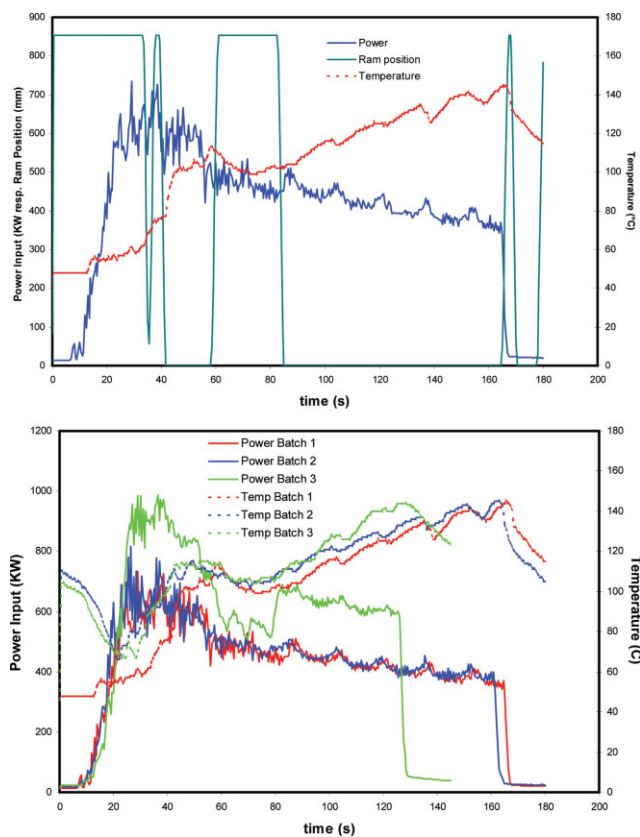


Figure 7 (a) Fingerprints of the first remilling process and (b) process variations of three subsequent batches (GK160 SUK with the old standard rotor design). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

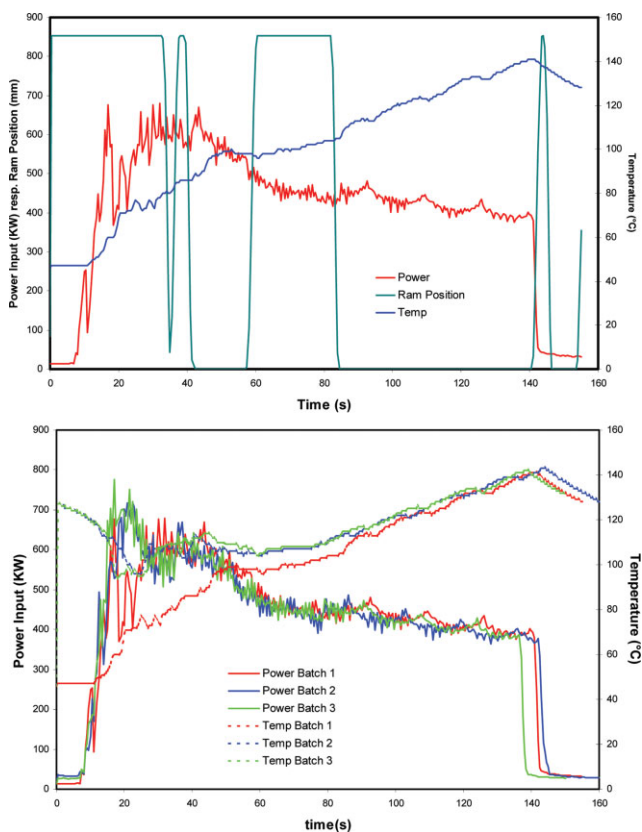


Figure 8 (a) Fingerprints of the second remilling process and (b) process variations of three subsequent batches (GK160 SUK with the old standard rotor design). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mixing process). Generally, the power input was higher for batch 3. The power dropped when the ram was lifted. The effect on the temperature increase can be clearly seen in Figure 7(b). Because the discharge criterion was based on temperature, the resulting mixing time was remarkably shorter than in batches 1 and 2. No clear explanation can be offered for this effect. Most probably, the weight of the master batch of batch 3 exceeded the target weight, but weight was unfortunately not recorded during this trial. An effect in the mixing quality was expected, although the silanization effect between the three batches during the first remixing process should have been more or less similar because the temperature of batch 3 was generally 5–10°C higher during the silanization phase, although the duration was shorter. (The silanization phase might be considered part of the mixing process when the temperature is higher than 120°C).

As expected, the fingerprints of the second remixing process looked very similar to the fingerprints of the first two batches from the first remixing process (see Fig. 8). The level of the power input was slightly higher (ca. 30–50 kW at the end of the mix-

ing process), which indicated that the viscosity development of the compound during mixing was slightly different. Probably, the remaining agglomerates of silica were broken down after the ram was moved down to its lowest position. Although the temperature was too low for a significant silanization effect during the first part of the process, the hydrophilic surfaces of the silica particles caused a temporary reinforcing effect. The fact that the singularity of batch number 3 of the first remixing process could not be recognized in the second remixing step is worth noting. Most likely, there was some homogenization occurring on the two-roll mills, downstream to the first remixing process, which was able to reduce batch-to-batch variations, because the two subsequent batches were partly blended. As the mixing process proceeded, the signal of the power input became more constant (a Doppler-like effect was recognized: every 20 s, the power input ran through a local maximum because of the conjugated orientations of the rotors).

In Figure 9, the fingerprints of the final-batch mixing are given. Because curatives were added, we had to prevent the compound from vulcanizing. For this reason, the compound temperature could not

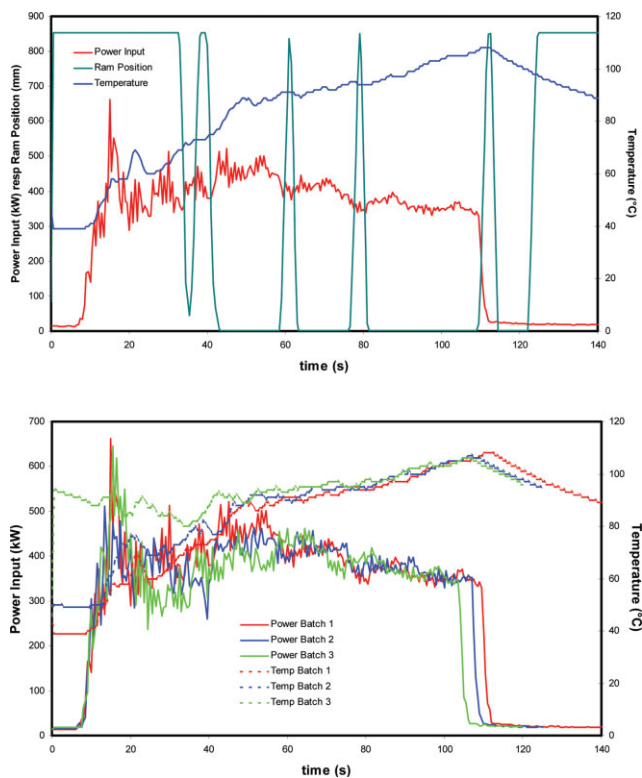


Figure 9 (a) Fingerprints of the final batch mixing process and (b) process variations of three subsequent batches (GK160 SUK with the old standard rotor design). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

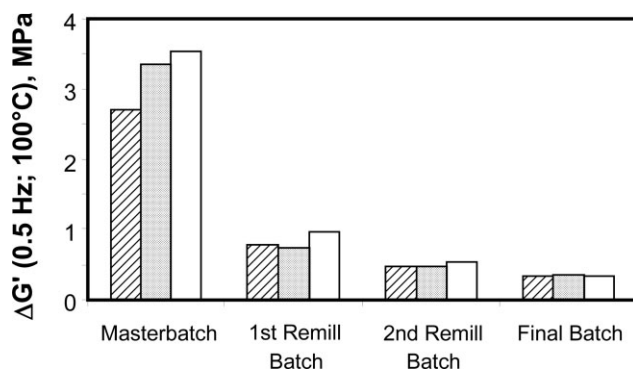


Figure 10 Dynamic stress softening results.

exceed 110°C. The use of a slightly lower fill factor could reduce the temperature increase. Therefore, the maximum power was lower compared with remixing (550 vs 700 kW). The presence of powdery materials (i.e., the curatives) at the beginning of the final mixing cycle (before they were incorporated into the matrix) also promoted a slightly lower power input. Diphenyl guanidine (DPG) was added to the final mix to cover the remaining hydrophilic silica surface because the silanization should have progressed up to a sufficient level before the curative system was added to the compound.

Laboratory testing

Test samples were taken randomly from the last two-roll mill in each production step. With a Rubber Process Analyzer, we assessed the dynamic stress softening, that is, the so-called Payne effect, of these samples (one result per batch) by means of measuring the drop-in modulus (either the complex modulus or G') when the strain (deformation) was increasing from a lowest to a highest value at a constant frequency and temperature. The results in terms of the G' difference (at 0.5 Hz and 100°C) when the strain varied from 0.02 to 20° are given in Figure 10.

Some trends were visible from the Payne effect measurements:

- Result scatter decreased as mixing proceeded. This was surely an effect of equalizing temperature gradients initially present in the rubber stock, which would vanish during the cooling process and the subsequent storage of the compound.
- The reduction of the Payne effect between the mixing steps was remarkable, especially between master-batch mixing and the first remixing. Most probably, the remaining silica agglomerates present in the master batch were dispersed during

the first remixing process, and this was followed by silanization. Also, after the second remixing, the Payne effect was reduced by another 40% (from 0.8 up to 0.5 MPa as an average).

- The reduction of the Payne effect between the second remixing and the final batch mixing process was still remarkable; however, it was most probably caused by the coverage of newly created silanol surfaces (because of an ongoing dispersion effect) with DPG.
- Some trends, observed in the fingerprints might have been correlated with the Payne effect observation as well; however, one should take the reproducibility of both sampling and measurement into account. The first master batch had the lowest Payne effect, maybe because of its highest mixing effect (longest mixing time.) The fingerprint of batch 3 of the first remixing deviated from the others, so did its Payne effect.

As we discuss in the second article of this series, more sophisticated Fourier transform rheometry experiments not only confirmed the previous observations but also provided additional information, which further confirmed the observations made with the instrumented mixers.

DISCUSSION

With respect to the dispersion mechanism proposed earlier in this article, the performance of the mixing line could be evaluated, and an outlook to further improvements could be deduced. After the fillers were added to the polymer blends, the dispersion process started, probably by means of a kind of grinding action rather than through high stresses, because immediate good wetting of hydrophilic particles by a hydrophobic rubber material is highly improbable. After the process oil and the silane were injected, the latter immediately migrated onto the hydrophilic silica surface, and as soon as the temperature was sufficiently high, the silanization process initiated. Sufficient conditions for the efficient incorporation of the filler system into the polymer matrix were gradually met as more and more hydrophobic silica particles appeared and as the process oil softened the rubber matrix. Increasingly, the mixing chamber content acted as a continuum, and further dispersion might have then resulted from high shear stresses between the rotor tips and chamber walls, as indeed was the case for carbon black mixing.¹⁴ However, because of the accompanying high power input and the rather poor cooling performance within the mixer chamber, the temperature of the compound rose and the viscosity was reduced. It follows that the reduction of the rotor speed might

have attenuated further temperature increases to control the silanization reaction. Both a rather high compound temperature and the corresponding low viscosity, combined with slow rotor speed, might have reduced the dispersion effect quite remarkably, and therefore, the effect on the quality of the mixture might have presented a kind of asymptotic behavior. Because temperature differences of 10–15° might have been present throughout the stock, the temperature increase during the silanization step should have been moderate. Future developments of the mixing cycle should, consequently, be based on a more aggressive temperature increase after the addition of the process oil, followed by a sufficiently long postmixing step to allow the silanization reaction to be as complete as possible.

After the compound was discharged onto the two-roll mills, a temperature equalizing effect was observed. The two-roll milling process is well known for its efficient distributive mixing effect, which allows blending between subsequent batches. When the rubber sheet was pulled through the stock blender, large surfaces were created, from which gaseous side products such as ethanol could evaporate from the matrix.

After the rubber compound was cooled and the next mixing process was started, the viscosity of the compound was high because of the low temperature. This favored a dispersing effect. The remaining silica clusters were then broken down, and the remaining free silane migrated to the newly created silica surfaces, where it reacted if and when the activation temperature was reached. The result was a boost in the silanization effect of the compound, as shown from the laboratory evaluation. This effect was previously reported by Gohl¹⁵ and Nijman et al.¹⁶

Basically, the effect of the second remixing process on the degree of silanization was lower compared with the effect of the first remixing step. However, the same mixing mechanism took place in both processes. Through the application of various rotor speeds during remixing, the dispersion effect and the silanization reaction can be distinguished to some extent. If rotor speed is high at the beginning, a more aggressive dispersion effect occurs before the silanization reaction becomes efficient. If the mixing process is conducted at a lower rotor speed (or better, if the rubber temperature is controlled by the adjustment of the rotor speed), isothermal mixing at 140°C, ideal for silanization, can be pursued. This remixing line was operated at a fixed rotor speed.

The only purpose of final batch mixing is to incorporate the curative system at temperatures compatible with scorch safety. Further silanization does not proceed significantly, and newly created hydrophilic silica surfaces, if any, are covered by DPG to improve the processability of the compound and to

avoid migration and adsorption of antioxidants or curatives to the silica surface.

CONCLUSIONS

During the preparation of silica-filled SSBR-based tread compounds, an *in situ* chemical reaction between a silanelike TESPT and the silanol groups on the silica surfaces had to take place. This chemical treatment was necessary, both to obtain a sufficiently high microdispersion level (associated with a low Payne effect) and to create chemical bonds between the filler and polymer.

The silanization reaction had to preferably take place at temperature levels between 140 and 150°C, but, on the contrary, filler dispersion needed a much lower temperature. Instead of mixing the compound for excessive time until the desired degree of silanization was achieved, it was, indeed, more efficient to dump, sheet off, cool, and then proceed through some remixing steps to use the relatively lower compound temperature at the beginning of such downstream processes for enhanced stress-induced dispersing effects.

The previous conclusions were well supported by the performance analysis of the silica–silane compounding line, thanks to the precise information provided by the so-called mixing signatures. As we show in the second article of this series, advanced rheological testing methods, such as Fourier Transform rheometry, on the one hand, totally support the previous conclusions and, on the other hand, bring additional information that sheds some light on the complexity of the dispersion and silanization processes as currently performed in the tire industry. It is clear that a better understanding of the mixing process of silica–silane compounds will open the way to the design of more efficient mixing procedures. However, a lot of research, both in laboratory- and industrial-sized mixers, is necessary, which will likely be associated with more intelligent mixing control strategies, to eventually obtain a very high batch uniformity, combined with efficient mixing and silanization processes.

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